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Surface Modification and Nanojunction Fabrication with Molecular Wires

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Electron transfer has been a core subject in science and technology. The overarching goal of this AOARD project is the development of molecular wires with metal-metal bonds, and ultimately devices based on the unique electron transporting behaviors across the nano-objects. One of the first steps is to tailor the axial ligands for the molecular wires, specifically, to make contact between molecules and the electrode. For the previous AOARD project (FA2386-12-1-4006), the Taiwan and US PI/co-PIs studied both metal string (EMAC) and diruthenium wires containing axial ligands suitable for attachment to gold and silica oxide surfaces. Platforms of conductance measurements for single-molecule studies were developed by the Taiwan team. The highlight of the current project period is the fabrication of high-performance top-gated nanowire molecular flash memory based on diruthenium wires (ACS Appl. Mater. Interfaces 2015, 7, 27306-27313). Additional work to be published investigates the charge trapping mechanism at molecule-oxide interfaces (J. Phys.: Condens. Mat. 2016, 28, In press).

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Surface Modification and Nanojunction Fabrication with Molecular Metal Wires

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Abstract
Electron transfer has been a core subject in science and technology. The overarching goal of this AOARD project is the development of molecular wires with metal-metal bonds, and ultimately devices based on the unique electron transporting behaviors across the nano-objects. One of the first steps is to tailor the axial ligands for the molecular wires, specifically, to make contact between molecules and the electrode. For the previous AOARD project (FA2386-12-1-4006), the Taiwan and US PI/co-PIs studied both metal string (EMAC) and diruthenium wires containing axial ligands suitable for attachment to gold and silica oxide surfaces. Platforms of conductance measurements for single-molecule studies were developed by the Taiwan team. The highlight of the current project period is the fabrication of high-performance top-gated nanowire molecular flash memory based on diruthenium wires (*ACS Appl. Mater. Interfaces* **2015,** *7*, 27306-27313). Additional work to be published investigates the charge trapping mechanism at molecule-oxide interfaces (*J. Phys.: Condens. Mat.* **2016**, *28*, In press).

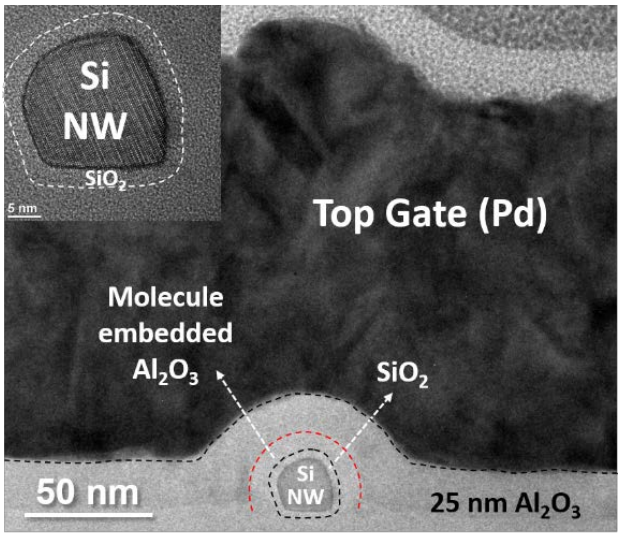
Introduction
The recent progress of molecular electronics has been manifested by the discovery of molecular properties such as conductance, rectification, and negative differential resistance. Further advancement requires a comprehensive understanding of the *I*–V characteristics to enable the development of molecular wires, voltage-gated switches, and single molecular transistors. Distinguished from other groups who typically concentrate on carbon-based organic molecules, diruthenium wires ($Ru_2(ap)_4$ and $Ru_2(DMBA)_4$) are our focus, where *ap* is 2-anilinopyridinate and DMBA is *N*,*N*-dimethylbenzamidinate. Metal alkynyl complexes have been considered as building blocks for molecular wires. Diruthenium units prepared in the PI's laboratory have been shown efficient electron/hole transport media (recent examples: *J. Am. Chem. Soc.* **2014,** *136*, 12174; *Angew. Chem. Int. Ed.* **2010**, *49*, 954). Our current effort focuses on further functionalization of these compounds to enable their attachment to both metallic, semiconductor (Si) and oxide surfaces through the capping group thiol, olefin and phosphonate, respectively. During the course of this project, both effective incorporation of diruthenium into metal-oxide / molecule / metal oxide junctions and resultant high performance memory devices have been demonstrated.

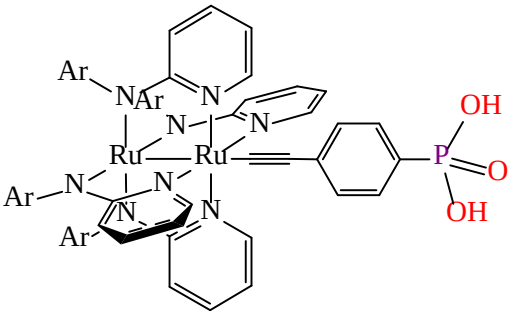
Results and Discussion:

Diruthenium compounds undergo multiple reversible one-electron oxidation / reduction processes, and are hence attractive candidates as the charge trapping sites in devices because they can access additional charged states in general. Both studies described below are excellent illustrations of this attribute, and especially noteworthy are the exceptional stability (> billion program-and-erase cycles) and multi-bit memory.

(1) *ACS Appl. Mater. Interfaces* **2015**, *7*, 27306-27313.
"Redox-Active Molecular Nanowire Flash Memory for High-Endurance and High-Density Non-Volatile Memory Applications".

In this work, high-performance top-gated nanowire molecular flash memory has been fabricated with redox-active molecules. Different molecules with one and two redox centers have been tested. The flash memory has clean solid/molecule and dielectric interfaces, due to the pristine molecular self-assembly and the nanowire device self-alignment fabrication process. The memory cells exhibit discrete charged states at small gate voltages. Such multi-bit memory in one cell is favorable for high density storage. These memory devices exhibit fast speed, low power, long memory retention, and exceptionally good endurance (> 10^9 PE cycles). The excellent characteristics are derived from the intrinsic charge-storage properties of the protected redox-active molecules. Such multi-bit molecular flash memory are very attractive for high-endurance and high-density on-chip memory applications in future portable electronics.





Embedded Active Molecues

Figure 1. (a, left) TEM image of the cross section of a ferrocene molecular flash memory dev ice. (b) The electro-active Ru_2 molecule incorporated.

(2) *J. Phys.: Condens. Mat.* **2016**, *28*, In press;
"Non-volatile Memory Devices with Redox-active Diruthenium Molecular Compound".

Non-volatile Flash-based memory devices,which incorporate a novel redox-active diruthenium molecule, is demonstrated. The memory device is in a capacitor structure, metal/oxide/molecule/oxide/silicon, where the diruthenium molecule is covalently attached to the oxide using a unique "click" chemistry attachment which serves two fold purposes: (1) ease of chemical design and synthesis, and (2) provides an additional spatial barrier between the oxide/silicon to the diruthenium molecule. The molecular memory devices display an unsaturated charge storage window, and we attribute this demonstration to the intrinsic

properties of the redox-active molecule. These molecular devices are very attractive for future non-volatile memory applications.

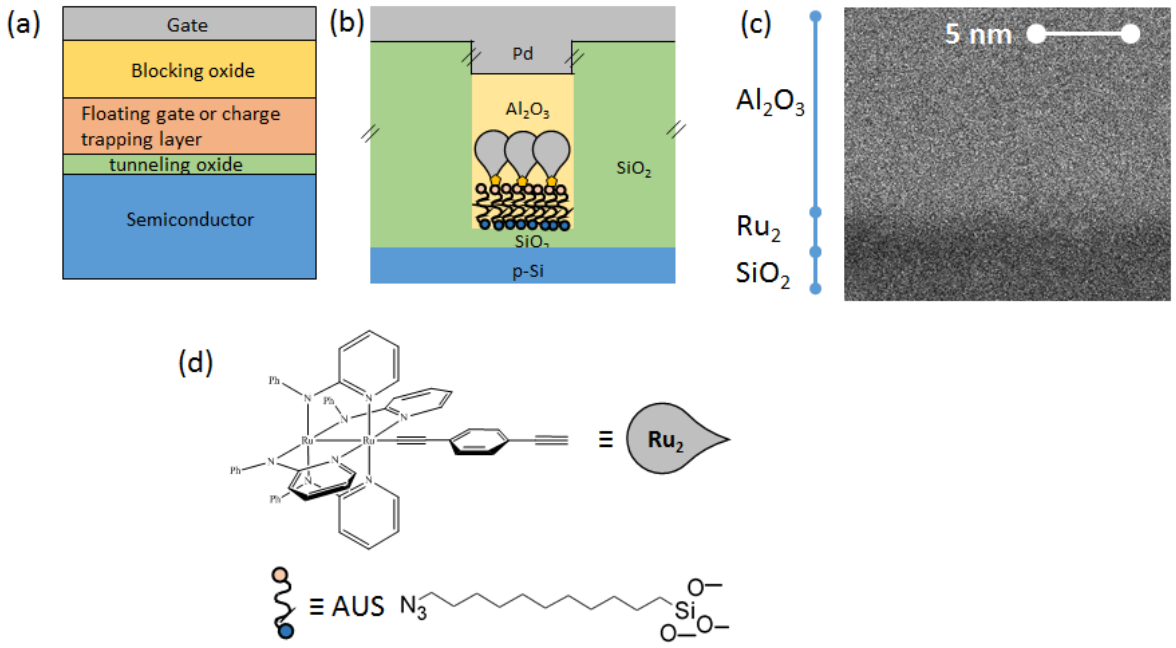


Figure 2. Schematic cross-sectional drawing (not to scale) of a (a) prototypical Flash-based memory device, (b) the molecular memory device in a capacitor structure used in this study, and (c) HAADF STEM image of the molecular interface between Al_2O_3 and SiO_2. An aliphatic linker (AUS) is chemically bonded to the SiO_2 tunneling layer and the Ru_2 layer is chemically tethered to the azide by "click" chemistry. In (d), the chemical structure of the redox-active Ru_2 and the aliphatic AUS are shown, and corresponding molecular cartoons are defined.

Concluding Remarks:

Two types of flash memory devices containing Ru_2 compounds as the charge storage species have been fabricated, and excellent performances demonstrated.

List of Publication:

Zhu, H.; Pookpanratana, S. J.; Bonevich, J. E.; Natoli, S. N.; Hacker, C. A.; Ren, T.; Suehle, J. S.; Richter, C. A.; Li, Q. *ACS Appl. Mater. Interfaces* **2015**, *7*, 27306-27313; "Redox-Active Molecular Nanowire Flash Memory for High-Endurance and High-Density Non-Volatile Memory Applications".

b) papers published in peer-reviewed conference proceedings, None

c) papers published in non-peer-reviewed journals and conference proceedings, None

d) conference presentations without papers, None

e) manuscripts submitted but not yet published,

Pookpanratana, S.; Zhu, H.; Bittle, E. G.; Natoli, S. N.; Ren, T.; Gundlach, D. J.; Richter, C. A.; Li, Q.; Hacker, C. A. *J. Phys.: Condens. Mat.* **2016**, *28*, In press; "Non-volatile Memory Devices with Redox-active Diruthenium Molecular Compound".

f) provide a list any interactions with industry or with Air Force Research Laboratory scientists or significant collaborations that resulted from this work. None

DD882: There is no material from this project required to fill in Form DD882 (the inventions disclosure form). The inventions disclosure form is submitted in a separate document.

Attachments: Publication 1.